Energy levels and extension of the Schrödinger operator.

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Abstract

Although energy levels are often given by solutions of the radial equation such that u(0) is non zero, and hence by first-order singular functions which are not eigenfunctions of H, the latter is always considered as the only operator that gives energy levels. Vibrational levels of diatomic molecules are a usual example. We show that the operator which has singular eigenfunctions, or pseudofunctions, that give energy levels, is the operator whose action on pseudofunctions amounts to the embedding in the distributions of R^3 of their Hamiltonian in $R^3/\{0\}$. When its eigenfunctions are regular, this operator amounts to H. Energy levels, which are given by eigenfunctions of H when u(0) is zero, are thus given in any case by eigenfunctions of this operator, which is an extension of the Schrödinger operator, but not of the Hamiltonian.

1 Introduction. Energy levels and radial equation.

In a central potential $\mathcal{V}(r)$ energy levels $\mathcal{E}_n$ are eigenvalues of the Hamiltonian that belong to normalized eigenfunctions $\psi_n = [w_n(r)/r]Y_\ell^\mu(\theta, \varphi)$ which behave at the origin like $r^\ell Y_\ell^\mu(\theta, \varphi)$, and hence eigenvalues of the radial equation that belong to normalized eigensolutions $w_n(r)$ which behave at the origin like $r^{\ell+1}$,

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + \mathcal{V}(r) \right] w_n(r) = \mathcal{E}_n w_n(r) \tag{1}$$

As physical potentials $\mathcal{V}(r)$ are not exactly known, one must substitute theoretical and then approximate potentials $V(r)$ for which the Hamiltonian has a discrete set of normalizable eigenfunctions $\Psi_n = [u_n(r)/r]Y_\ell^\mu(\theta, \varphi)$, and

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hence the radial equation a discrete set of normalizable analytic eigensolutions $u_n(r)$ which behave at the origin like $r^{\ell+1}$,

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r)\right]u_n(r) = E_n u_n(r) \tag{2}$$

One assumes indeed that if $V(r) \approx \mathcal{V}(r)$, Ψ_n will be similar to ψ_n, $u_n(r)$ to $w_n(r)$, and $E_n \approx \mathcal{E}_n$. The solutions of the radial equations, which are written in the form of series, $u_n(r) = r^\lambda \sum_{k \geq 0} a_k^n r^k$, are given in $\mathrm{R}^3/\{0\}$ by both roots $\lambda = \ell+1$, and $\lambda = -\ell$, but in R^3 for $\ell > 0$ only by the root $\lambda = \ell+1$ [1]. These solutions are normalizable and give, when substituted in Ψ_n, eigenfunctions of H, or solutions of the Schrödinger equation. For $\ell = 0$ the radial equations

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \mathcal{V}(r)\right]w_n(r) = \mathcal{E}_n w_n(r) \tag{3}$$

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V(r)\right]u_n(r) = E_n u_n(r) \tag{4}$$

have solutions in R^3 given by both roots, that is, $\lambda = 1$, and $\lambda = 0$. Both roots give normalizable solutions, but only the solutions given by the root $\lambda = 1$ give, when substituted in Ψ_n, solutions of the Schrödinger equation [1]. Insofar as energy levels $\mathcal{E}_n$ are eigenvalues of the Hamiltonian, the solutions $w_n(r)$ of (3) behave at the origin like r. In order for Ψ_n to be eigenfunctions of H, one must substitute potentials $V(r)$ for which the following conditions must be satisfied:
i) $V(r)$ must be close to $\mathcal{V}(r)$, at least in the neighborhood of the minimum;
ii) Eq.(4) must have a discrete set $u_n(r)$ of normalizable analytic solutions ;
iii) these solutions must behave at the origin like r.

Now, explicit analytic solutions of (4) can be derived only for a limited number of potential energy functions $V(r)$. When we demand that the first two conditions be satisfied, this number is much more limited. If we moreover demand that these solutions behave at the origin like r, the problem cannot necessarily be solved. This is why one substitutes potentials $V(r)$ close to $\mathcal{V}(r)$, for which (4) has a discrete set of normalizable solutions *regardless of their value at the origin*. One intuitively expects indeed that if $V(r) \approx \mathcal{V}(r)$ and if (4) has a discrete set of normalizable solutions $u_n(r)$, moreover demanding that they behave at the origin like r is a *supplementary* condition that is *not required* to obtain eigenvalues E_n of (4) close to the eigenvalues $\mathcal{E}_n$ of (3). This is shown by the following example.

2   Vibrational levels of diatomic molecules.

The vibrational levels of diatomic molecules are of the form

$$\mathcal{E}_n = -V_m + (n+\tfrac{1}{2})\hbar\omega + C_2(n+\tfrac{1}{2})^2 + C_3(n+\tfrac{1}{2})^3 + ... \qquad n = 0,1,2...$$

In the Born-Oppenheimer approximation the potential energy of interaction between the two nuclei of a diatomic molecule is a central potential $V(r)$, attractive at large distances, repulsive at short distances, with a minimum at $r = r_m$. By expanding the potential in powers of $r - r_m$ in the neighborhood of the minimum by neglecting the terms of order ≥ 3, it gives

$$V(r) = \tfrac{1}{2}m\omega^2(r - r_m)^2 - V_m \qquad \omega = [V''(r_m)/m]^{1/2} \qquad (5)$$

This parabolic potential is used as a first approximation, which holds in the neighborhood of the minimum, and then gives the first levels. The radial equation for $\ell = 0$ involving this potential,

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \tfrac{1}{2}m\omega^2(r - r_m)^2 - V_m \right] u_n(r) = E_n u_n(r) \qquad (6)$$

has the square integrable solutions and the corresponding eigenvalues

$$u_n(r) = N_n exp\left[-\tfrac{1}{2}\beta^2(r - r_m)^2 \right] H_n[\beta(r - r_m)] \qquad \beta^2 = m\omega/\hbar$$

$$E_n = (n + \tfrac{1}{2})\hbar\omega - V_m \qquad\qquad n = 0, 1, 2... \qquad (7)$$

where H_n are Hermite polynomials of order n and N_n normalization constants. Experimental data show that these eigenvalues give estimates of the first vibrational levels of most molecules. Now, except for the case where βr_m coincides with a zero of H_n,

$$u_n(0) = N_n exp(-\tfrac{1}{2}\beta^2 r_m{}^2)H_n(\beta r_m) \neq 0 \qquad (8)$$

Analytical forms for $V(r)$ closer to the realistic physical potential have been proposed, the most frequently used is the Morse potential [2]

$$V_M(r) = V_m\{exp[-2a(r - r_m)] - 2exp[-a(r - r_m)]\} \qquad (9)$$

For $\ell = 0$ the square-integrable solutions and the eigenvalues of the radial equation are [2]

$$u_n(r) = exp[-z(r)/2][z(r)]^{b/2} L_{n+b}^b[z(r)]$$

$$z = 2d\,exp[-a(r - r_m)] \qquad d = (2mV_m)^{\frac{1}{2}}(a\hbar)^{-1} \qquad b = 2d - 1 - 2n$$

$$E_n = (n + \tfrac{1}{2})\hbar - (n + \tfrac{1}{2})^2(\hbar^2\omega^2/4V_m) - V_m \qquad \omega = a(2V_m/m)^{\frac{1}{2}}$$

where $L_{n+b}^b(z)$ are generalized Laguerre polynomials. Experimental data show that these eigenvalues give very accurate values for the vibrational levels of nearly all molecules, but again the condition $u_n(0) = 0$ is not satisfied.

If one considers that by substituting the potential (5) "we are left with the equation of a one-dimensional harmonic oscillator centered at $r = r_m$" [3,A$_{\text{V}}$], no boundary condition is required at the origin, so that in particular perturbation theory for a one-dimensional harmonic oscillator is applied to the third-order term.

Otherwise, arguments have been proposed to justify that the fact that $u_n(0) \neq 0$ is of no significance. According to Pauling *et al.* the solutions of the radial equation must be zero at $r = 0$ and $+\infty$, whereas the solutions of the harmonic oscillator must be zero at $r = -\infty$ and $+\infty$, but because of the rapid decrease in the harmonic oscillator functions outside the classically permitted region, "it does not introduce a serious error to consider that the two sets of boundary conditions are practically equivalent" [4, See also 5,6,7]. As noted by Schiff, the eigenvalues of the radial equation are those of a linear harmonic oscillator "if the domain of r is extended to $-\infty$" [8], which amounts to substituting a one-dimensional problem for a three-dimensional problem. Or else, one considers that, as (6) is the radial equation for zero angular momentum states, the exact solutions must be rigorously zero at $r = 0$, but the solutions (7) are "practically zero at the origin" [3,F$_{\text{VII}}$]. It should be noted that one often considers indeed that the exact solutions of (6) can be obtained only if the variable is taken from $-\infty$ to $+\infty$, or if the solutions vanish at the origin. In fact, (7) are the exact solutions of (6), that is, the solutions in R^3 ($r \geq 0$), as is easily checked.

Similarly, the value of the Morse potential is sometimes considered as so large at $r = 0$ that the Morse eigenfunctions are "effectively zero for $r < 0$" [9]. In fact they are non zero at $r = 0$, but according to Morse since "in every case $r\Psi$ will be extremely small ... this discrepancy will not affect the values of the energy levels" [2, See also 6,7].

But if the two boundary conditions, $u_n(0) = 0$ and $u_n(0) \approx 0$, are practically equivalent, it merely means that the former condition is not required. First-order singular functions are not indeed "practically eigenfunctions" of H, they are eigenfunctions of H in R^3/{0}, but not in R^3. In other words, whether or not $u(0)$ is very small, if it is non zero, Ψ_n behaves at the origin like $1/r$, and what these examples show is thus that energy levels are not affected because that they are not given by eigenfunctions of H. By *changing the condition at the origin, we change indeed the operator.*

3   The energy levels and the operator H_d.

We must thus determine the operator which has singular eigenfunctions of the form $\Psi_n = [u_n(r)/r]Y_\ell^\mu(\theta, \varphi)$ and corresponding eigenvalues E_n, such that for $\ell = 0$ $u_n(r)$ and E_n are solutions of (4) with $u_n(0) \neq 0$. Now, when Ψ_n and $u_n(r)$, which are of C$^\infty$(R^3/{0}), are singular at the origin, they define in R^3 distributions called pseudofunctions, denoted by Pf.Ψ_n and Pf.$u_n(r)$ [10], and the latter are not a solution of (2) [1]. The radial equation which has in R^3 singular solutions Pf.$u_n(r)$ given by the root $\lambda = -\ell$ is the *extension* in R^3 of

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(2), it is the equation [1]

$$\text{Pf.} \left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r) \right] u_n(r) = E_n \text{Pf.} u_n(r) \qquad (10)$$

Its solutions, given by both roots $\lambda = \ell+1$ and $\lambda = -\ell$, are either functions $u_n(r)$ which behave at the origin like $r^{\ell+1}$, or pseudofunctions $\text{Pf.} u_n(r)$ which behave at the origin like $\text{Pf.} r^{-\ell}$. (The symbol Pf. is used when we have either the former or the latter). When the solutions of (10) are given by the roots $\lambda = \ell+1$ and $\lambda = 0$ (i.e. $\lambda = -\ell$ for $\ell = 0$), the symbol Pf. is useless and (10) is written in the form (2). Just as Ψ_n defines in R^3 the pseudofunction $\text{Pf.} \Psi_n = \text{Pf.} [u_n(r)/r] Y_\ell^\mu(\theta, \varphi)$, its Hamiltonien in $\text{R}^3/\{0\}$, which is the Hamiltonian in the sense of the functions

$$H\Psi_n = \frac{1}{r} \left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r) \right] u_n(r) Y_\ell^\mu(\theta, \varphi) \qquad r > 0$$

defines in R^3 the distribution

$$\text{Pf.} H\Psi_n = \text{Pf.} \left\{ \frac{1}{r} \left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r) \right] u_n(r) Y_\ell^\mu(\theta, \varphi) \right\} \qquad (11)$$

Let H_d the operator whose action on a pseudofunction $\text{Pf.} \Psi_n$ amounts to the embedding in the distributions of R^3 of the Hamiltonian of Ψ_n in $\text{R}^3/\{0\}$,

$$H_d \text{Pf.} \Psi_n = \text{Pf.} H\Psi_n \qquad (12)$$

If $\text{Pf.} u_n(r)$ is a solution of (10), whether it is given by the root $\lambda = \ell + 1$, or by the root $\lambda = -\ell$, by substituting (10) in (12), we obtain the eigenvalue equation of H_d,

$$H_d \text{Pf.} \Psi_n = E_n \text{Pf.} \Psi_n \qquad (13)$$

where E_n is the eigenvalue of (10) that belongs to $\text{Pf.} u_n(r)$.

The *normalizable* solutions are given by the roots $\lambda = \ell+1$ $\forall \ell$, and $\lambda = 0$, that is, $\lambda \in N$. As they are less singular at the origin than $1/r^3$, the symbol Pf. can be dropped [10], and (13) is written

$$H_d \Psi_n = E_n \Psi_n \qquad \lambda \in N \qquad (14)$$

In particular for $\ell = 0$, $\Psi_n = (4\pi)^{-1/2}[u_n(r)/r]$, whether $u_n(0) = 0$ if $\lambda = 1$, or $u_n(0) \neq 0$ if $\lambda = 0$, in *both* cases

$$H_d \frac{1}{\sqrt{4\pi}} \frac{u_n(r)}{r} = \frac{1}{\sqrt{4\pi}} E_n \frac{u_n(r)}{r} \qquad \lambda = 0 \qquad (15)$$

where $u_n(r)$ and E_n are solutions of the radial equation (4). H_d is thus the *required operator.*

In order to compare the operators H_d and H, let us recall that the Hamiltonian of $\text{Pf.}\Psi_n = \text{Pf.}r^{\lambda-1}\sum_{k\geq 0}a_k^n r^k Y_\ell^\mu(\theta,\varphi)$ is the Hamiltonian in the sense of the distributions given by [1]

$$H\text{Pf.}\Psi_n = \text{Pf.}\left\{\frac{1}{r}\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r)\right]u_n(r)Y_\ell^\mu(\theta,\varphi)\right\} - \frac{\hbar^2}{2m}Q_{\lambda,\ell}(\delta)$$

$$Q_{\lambda,l}(\delta) = \sum_{k=0}^{-\lambda}a_k\chi_{p(k)}B_{\ell,p(k)}C_{p(k)}\,r^\ell\,Y_\ell^\mu(\theta,\varphi)\Delta^{p(k)}\delta \qquad p = -\frac{k+\lambda-\ell}{2}$$

$$\chi_p = \begin{cases}1 & if\ p \in N \\ 0 & if\ p \notin N\end{cases} \qquad B_{\ell,p} = \frac{1-2\ell}{4p+1} \qquad C_p = -\frac{(4p+1)\pi^{3/2}}{2^{2p-1}p!\,\Gamma(p+3/2)} \quad (16)$$

where Δ^p is the iterated Laplacian, δ the Dirac mass, where the even, resp. odd, terms of the sum are zero , if $\lambda - \ell$ is odd, resp. even, and where $Q_{\lambda,\ell}(\delta)$ $\neq 0$ if and only if there is at least one coefficient $a_k \neq 0$ for which $k + \lambda - \ell$ is an even negative integer [1]. As

$$(H_d - H)\text{Pf.}\Psi_n = [\text{Pf.}, H]\,\Psi_n = \frac{\hbar^2}{2m}Q_{\lambda,\ell}(\delta) \tag{17}$$

the operators H_d and H differ when they act on pseudofunctions for which the operators Pf. and H do not commute, or for which $Q_{\lambda,\ell}(\delta) \neq 0$. Considering that energy levels are given in any case by the operator H amounts to identify the operators H_d and H, and hence to take no account of the noncommutation of the operators Pf. and H. As the operators H_d and H are equivalent in $\text{R}^3/\{0\}$, and in R^3 when the Laplacian is the Laplacian in the sense of the functions, it comes from the confusion between the Laplacians in $\text{R}^3/\{0\}$ and in R^3, or/and between the Laplacians in the sense of the functions and in the sense of the distributions [11]. By substituting (10) in (16), we obtain

$$H\text{Pf.}\Psi_n = E_n\text{Pf.}\Psi_n - \frac{\hbar^2}{2m}Q_{\lambda,\ell}(\delta) \tag{18}$$

When the solutions of the radial equation are given by the root $\lambda = \ell + 1$, $p = -(k+1)/2 \notin N\ \forall k$, so that $Q_{\ell+1,\ell} = 0$, Ψ_n behaves at the origin like $r^\ell Y_\ell^\mu(\theta,\varphi)$, it is an eigenfunction of H. When the solutions of the radial are given by the root $\lambda = -\ell$, as $a_o \neq 0$ and $p = \ell \in N$ for $k = 0$, $Q_{-\ell,\ell} \neq 0$, $\text{Pf.}\Psi_n$ behaves at the origin like $\text{Pf.}r^{-(\ell+1)}Y_\ell^\mu(\theta,\varphi)$, it is not an eigenfunction of H [1]. As $Q_{0,0} = -\sqrt{4\pi}u_n(0)\delta$, in the case of normalizable solutions (18) is written

$$H\Psi_n = E_n\Psi_n \qquad\qquad \lambda = \ell + 1$$

$$H\frac{1}{\sqrt{4\pi}}\frac{u_n(r)}{r} = \frac{1}{\sqrt{4\pi}}E_n\frac{u_n(r)}{r} + \frac{\hbar^2\sqrt{\pi}}{m}u_n(0)\delta \qquad\qquad \lambda = 0 \qquad (19)$$

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Comparison between (14), (15) and (19) shows that *energy levels, which are given by eigenfunctions of H when $u_n(0) = 0$, are given in any case by eigenfunctions of H_d.*

4 The Hamiltonian, the Schrödinger operator and the operator H_d.

The differential form

$$H = -\frac{\hbar^2}{2m}\Delta + V \qquad (20)$$

is usually called Hamiltonian or Schrödinger operator. Now, a differential form such as (20) defines an operator only on a given class of functions, so that the same differential form can define different operators [See e.g. 12]. Any function Ψ, or pseudofunction Pf.Ψ, belongs to the domain $\mathcal{D}$ on which the Hamiltonian, denoted by H, is defined by (20). On the other hand, the operator involved in the Schrödinger equation, or Schrödinger operator, denoted by H_s, can be defined on the set $\mathcal{D}_s$ of the functions which are any superpositions of eigenfunctions of H. As $\mathcal{D}_s$ is a subset of $\mathcal{D}$, and as the two operators are equivalent on $\mathcal{D}_s$, that is, $H\Psi \equiv H_s\Psi$ if $\Psi \in \mathcal{D}_s$, the Schrödinger operator is a *restriction* of the Hamiltonian. As long as one confines oneself to solutions of the Schrödinger equation, these two operators, which have the same eigenfunctions, are equivalent, so that the distinction is not necessary, and in fact it is not made. Nevertheless the distinction can be made with respect to the operator H_d.

The latter is defined on the same domain $\mathcal{D}$ as H. Moreover (13) and (18) show that the eigenfunctions of H, or of H_s, form a subset of the eigenfunctions of H_d, so that if $\Psi \in \mathcal{D}_s$, then $H_d\Psi \equiv H_s\Psi$. The operator H_d is thus also an extension of the Schrödinger operator. But the fact that the eigenvalue equation of H_d is an extension of the eigenvalue equation of H to the pseudofunctions such that $Q_{\lambda,\ell}(\delta) \neq 0$ does not mean that H_d is an extension of H. Eq.(17) shows indeed that they are different when $Q_{\lambda,\ell}(\delta) \neq 0$, or when the operators Pf. and H do not commute. It follows that *the operators H and H_d are two different extensions of the Schrödinger operator.*

The condition for the operator H (and then H_s) to be self-adjoint is usually written $u(0) = 0$. However, according to Merzbacher the condition that the Hamiltonian must be self-adjoint implies that any two physically admissible eigensolutions of (2) must satisfy the condition [13]

$$\lim_{r\to 0}\left(u_1^*\frac{du_2}{dr} - u_2\frac{du_1^*}{dr}\right) = 0 \qquad (21)$$

This condition is satisfied, either for $u(0) = 0$ and $u'(0) \neq 0$, in which case Ψ is an eigenfunction of H_d and of H, or for $u'(0) = 0$ and $u(0) \neq 0$, in which case Ψ is an eigenfunction of H_d, but not of H. It follows that (21) is in fact the condition for H_d to be self-adjoint.

The operator H_d can also be defined, by using the linearity of the operator Pf., from the operator Pf.Δ introduced in [11]. As

$$\text{Pf.}H = \text{Pf.}(-\frac{\hbar^2}{2m}\Delta + V)$$

by similarly defining the operator Δ_d as

$$\Delta_d \text{Pf.}\Psi = \text{Pf.}\Delta\Psi \qquad (22)$$

we have

$$H_d = -\frac{\hbar^2}{2m}\Delta_d + V$$

5 A physically not required condition.

The boundary condition $u_n(0) = 0$ is definitely stated as a condition required to obtain energy levels because it is the condition for Ψ_n to be an eigenfunction of the Hamiltonian, but in practice this condition is not respected. It can be imposed when the solutions are determined with the help of numerical or approximation methods, but not when energy levels are determined with the help of analytic solutions.

In the case of diatomic molecules, in the parabolic like in the Morse potential, the fact that $u_n(0) \neq 0$ is regarded as of no significance owing to the fact that the origin being some distance outside of the classically allowed region, $u_n(0)$ is "very small". As the parabolic potential (5) is an expansion of the potential in the neighborhood of the minimum by neglecting the terms of order higher than 2, it remains close to the physical potential only in the neighborhood of the minimum. The Morse potential (9) is closer to the physical potential, and in a region more extended on both sides of the minimum. Comparison between the measured vibrational levels $\mathcal{E}_n$ and the eigenvalues E_n of the radial equations involving these potentials shows that the agreement between these eigenvalues and the energy levels decreases with n, and that the number of eigenvalues which are close to energy levels is all the greater as the region in which $V(r) \approx \mathcal{V}(r)$ is more extended. It means that this agreement essentially depends on $u_n(r)$ in the region where $V(r)$ is close to $\mathcal{V}(r)$, where one therefore expects that $u_n(r)$ is close to $w_n(r)$, the region where nearly the whole wave function is concentrated. It follows that if energy levels are not affected by the fact that $u_n(0) \neq 0$, it does not come from the fact that $u_n(0)$ is "very small", but from the fact that the origin is outside of the region where $V(r) \approx \mathcal{V}(r)$, where $u_n(r) \approx w_n(r)$, and where the wave function is concentrated, that is, in a region where $u_n(r)$ has little or none influence on the fact that E_n is close or not to $\mathcal{E}_n$.

Besides, in the case of the potential (5) $u_n(r)$ always vanishes *inside* of the classically allowed region. It means in particular that the condition $u_n(0) = 0$ can be satisfied only inside of this region.

Consider a physical potential $\mathcal{V}_o(r)$, and a supplementary potential, or a perturbation, $\mathcal{W}(r)$, for which one substitutes the spherical oscillator $V_o(r) = \frac{1}{2}m\omega^2 r^2$ and the linear potential $W(r) = -Cr$, so that the approximation of the physical potential $\mathcal{V}(r) = \mathcal{V}_o(r) + \mathcal{W}(r)$ is the potential $V(r) = V_o(r) + W(r)$ of the form (5), that is,

$$V(r) = \tfrac{1}{2}m\omega^2 r^2 - Cr = \tfrac{1}{2}m\omega^2(r - r_m)^2 + V_m$$

$$r_m = C/m\omega^2 \qquad V_m = C^2/2m\omega^2 \qquad (23)$$

As C and then r_m have any values, the origin is or not outside of the classically permitted region. When βr_m coincides with a zero of a Hermite polynomial of order N, that is, $H_N(\beta r_m) = 0$, then $u_N(0) = 0$, but $u_n(0) \neq 0$ for $n < N$. Insofar as the agreement between the eigenvalues of the radial equation and the energy levels decreases with n, the eigenvalues E_n with $n < N$ that belong to solutions $u_n(r)$ which do not satisfy the condition $u_n(0) = 0$ must be closer to an energy level than E_N that belongs to a solution $u_N(r)$ which satisfies this condition. The latter then cannot be considered as the condition required to obtain accurate, or better estimates of energy levels.

In the absence of supplementary potential, or of perturbation, the approximation of the physical potential is the spherical oscillator, $\mathcal{V}(r) \approx V(r)$, with

$$V(r) = \tfrac{1}{2}m\omega^2 r^2$$

$$u_n(r) = N_n exp(-\tfrac{1}{2}\beta^2 r^2)H_n(\beta r) \qquad E_n = (n + \tfrac{1}{2})\hbar\omega$$

$$u_n(0) = N_n H_n(0)$$

As Hermite polynomials satisfy the condition $H_{2p}(0) \neq 0$, $H_{2p+1}(0) = 0$, half the square-integrable solutions of the radial equation satisfy the condition $u_n(0) = 0$, and hence half the energy levels are given by eigenvalues of H. If the supplementary potential, or the perturbation, is a 1D potential $\mathcal{W}(x)$ for which one substitutes the linear potential $W(x) = -Cx$, the potential $V(r) = V_o(r) + W(x)$ used as an approximation of the physical potential $\mathcal{V}(r) = \mathcal{V}_o(r) + \mathcal{W}(x)$ is still a spherical oscillator, that is,

$$V(\rho) = \tfrac{1}{2}m\omega^2 r^2 - Cx = \tfrac{1}{2}m\omega^2\rho^2 - V_m$$

$$\rho = \left[(x - C/m\omega^2)^2 + y^2 + z^2\right] \qquad V_m = C^2/2m\omega^2$$

Half the energy levels are still given by eigenvalues of H. But when the supplementary potential, or the perturbation, is the 3D potential $\mathcal{W}(r)$ for which one substitutes the linear potential $W(r) = -Cr$, the potential used as an approximation of the physical potential is the potential (23), so that the solutions of the radial equation, which are given by (7), do not satisfy the

condition $u_n(0) = 0$, and then that the energy levels are not given by eigenvalues of H, as it is the case for diatomic molecules. It shows that whether or not energy levels are given by eigenvalues of H only depends on the potential used as an approximation of the physical potential – and hence on the latter.

Perturbation methods, in particular variational methods, apply to the eigenfunctions of H on which the theory is based. By substituting H_d for H these methods are extended to the eigenfunctions of H_d which behave at the origin like $1/r$. It is in agreement with the fact that energy levels are obtained with the help of such functions. Similarly, situations which are described with the help of functions which behave at the origin like $1/r$, require, to hold in R^3, and not only in $R^3/\{0\}$), that one substitutes H_d for H. This is the case of ingoing, outgoing and standing spherical waves which are described with the help of Green functions. As the latter behave at the origin like $1/r$, they are eigenfunctions of H in $R^3/\{0\}$), but not in R^3, so that this description does not hold at the origin, which is physically unsatisfactory. As Green functions are eigenfunctions of H_d in R^3, by substituting this operator, the description of spherical waves in terms of Green functions holds in the whole space.

Moreover, wave functions divergent at the origin, but normalizable, are encountered in the relativistic theory of the hydrogen atom. As the relativistic generalization of the Schrödinger equation is the Klein-Gordon equation which governs the wave function in the absence of electromagnetic field for a relativistic particle with spin zero, if the Laplacian must be taken in the sense of the distributions in this equation, one will be similarly led to substitute for Δ the operator Δ_d defined in (22).

6 Conclusion.

One usually considers, by putting forward different arguments, that the resolution of the Schrödinger equation must be supplemented with the boundary condition $u_n(0) = 0$, but when this condition is not satisfied, one admits, by putting forward other arguments, that this is of no significance. In fact the resolution of the Schrödinger equation need not be supplemented with any boundary condition [1], but the fact that the condition $u_n(0) = 0$ is not satisfied is significant, since it means, whether or not $u_n(0)$ is very small, that energy levels are not given by solutions of the Schrödinger equation. As energy levels are obtained by substituting theoretical and then approximate potentials, it should be taken for granted that in approximate solutions the boundary condition $u_n(0) = 0$, and hence the operator H, or H_s, are not required to obtain energy levels, and hence that the operator H_d, less stringent, is sufficient. The point is that the only potentials that are exactly known, and then used to obtain energy levels, are theoretical and then approximate potentials.

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